Title: Fundamental Investigation of Fuel Transformations in Advanced Coal Combustion and Gasification Processes

Authors: Robert H. Hurt, Joseph C. Calo
Todd Lang, Diane Lopez, Andrew Lamb
Brown University
Providence, RI 02912
Tel: 401 863-2685
Fax: 401 863-9210
E-mail: Robert_Hurt@brown.edu

Thomas Fletcher
Michael Clark, Dong Zheng
Brigham Yong University
Provo, UT

Alan Sayre
McDermott Technologies Inc.
Alliance, OH

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Abstract

The goal of this project is to experimentally characterize the high-temperature transformations of coals and alternative solid fuels over a wide range of operating conditions in temperature, pressure, and gas environment. The project will provide the database needed to extend existing submodels of pyrolysis and char burnout to the new conditions anticipated in next-generation energy technologies. The project team is using a combination of high-pressure TGA, atmospheric entrained flow reactor experiments, and experiments with a high pressure drop tube furnace to address volatile release, nitrogen release, inorganic release, and char properties and reactivity, with particular emphasis on gasification environments under pressure and enhanced oxygen environments at atmospheric pressure. The CPD and CBK models will be validated against full-scale data on current pc-technologies with industry involvement (McDermott/B&W) and will be extended to the new conditions using the data generated in the experimental portion of the program. To achieve the above project objective, a multi-university/joint industry team has been assembled, consisting of Brown University (PIs Robert Hurt and Joseph Calo), Brigham Young University (PI Thomas Fletcher), and McDermott's Babcock and Wilcox Power Generation Group (PI Alan Sayre).

Progress on the project to date can be summarized as follows. At Brown University, a new 3-step kinetic model for char oxidation has been developed that is robust enough to predict burning rates over wide ranges in temperature and oxygen pressure, yet simple enough for implementation in multi-dimensional CFD codes. The development of the model is described in a *Combustion and Flame* article that appeared in 2001 and has been implemented in code form as CBK/E. This is an extended (/E) version of the older CBK model, that includes high pressures char properties, the 3-step kinetic model, and improved documentation. Also at Brown, a large comparative study has just been completed of the combustion properties of chars from diverse coals and alternative solid fuels. Char combustion

reactivities at 500°C in air were determined for a set of over 30 starting materials. These reactivities varied over 4 orders of magnitude for the chars prepared at 700°C, and over 3 orders of magnitude for the chars prepared at 1000°C. The resultant reactivities correlate poorly with organic elemental composition and with char surface area. Specially-acquired model materials with minute amounts of inorganic matter exhibit low reactivities that fall in a narrow band as a function of wt-% carbon. Reactivities in this sample subset correlate reasonably well with total char surface area. A hybrid chemical/statistical model was developed which explains most of the observed reactivity variation based on four variables: the amounts of nano-dispersed K, nano-dispersed (Ca+Mg), elemental carbon (wt-% daf), and nano-dispersed vanadium, listed in decreasing order of importance. Catalytic effects play a very significant role in the oxidation of most practical solid fuel chars. Some degree of reactivity estimation is possible using only elemental analyses of parent fuels, but only if correlative techniques make use of the existing body of knowledge on the origin, form and dispersion of inorganic matter in various fuel classes.

McDermott Technologies has implemented both the CBK and CPD models into its in-house CFD codes and tested their performance. This work was done prior to the extension of the models for high pressure, in order to allow validation against the existing simple submodels, which were all developed for atmospheric operation and for which there is extensive experience with their application to design and retrofit jobs at full scale.

At BYU, a pressurized, entrained-flow reactor has been retrofitted with a flat-flame burner in order to perform coal pyrolysis experiments. The purpose of this experimental work is to determine the influence of pressure during pyrolysis on the properties of the resulting chars. This particular experiment has very high particle heating rates, which may be important for depicting swelling properties in industrial applications. Pyrolysis experiments at varied pressures (up to 10atm) are being performed on two coals: Pitt #8 hva-bituminous coal, and Knife River lignite. Char reactivities were determined using a high pressure TGA operated at the char formation pressure. The physical structures of the chars were explored using scanning electron microscopy and N_2 BET surface areas. The mass loss from pyrolysis was found using ash, Ti, and Al tracers. Elemental compositions of the chars were also measured. The completed data set will provide better information on the effects of pressure on pyrolysis yields as well as on char structure and reactivity.

Finally, back at Brown in the laboratory of P.I. Calo, a DMT High Pressure/High Temperature TGA has been used to obtain data on carbon dioxide gasification of two chars: Wyodak subbituminous coal char and a resin char. Gasification data were obtained from atmospheric pressure to 15 bar, and temperatures from 825°C to 1050°C. The results for the resin char indicate that the apparent activation energy *decreases* with *increasing* pressure. In addition, higher pressure increases reactivity at low temperatures, but this effect decreases with increasing temperature. These data are believed to reflect the behavior of the population of intermediate oxygen surface complex populations with pressure and temperature. Qualitatively similar effects were not apparent for the Wyodak subbituminous coal char. That is, the apparent reactivity and activation energy seemed to be relatively invariant with CO_2 pressure. The behavior of the latter is attributed to the catalytic effect of mineral matter in the coal char that favorably competes with the more intrinsic carbon mechanism on the resin char, as we have previously observed in related work. Experiments are continuing with the effects of varying partial pressures of CO and CO_2. It is also planned to measure the reactivity behavior of chars produced at high heating rates and high pressures at BYU.

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Papers and Presentations

Fletcher, Zeng, D., and W. C. Hecker, "High Pressure Reactivities of High Pressure Coal Chars," accepted for presentation at the 12th International Conference on Coal Science, Cairns, Australia (November, 2003).

Fletcher, T. H., D. Zeng, M. Clark, B. Crenshaw, and W. C. Hecker, "High Pressure Coal Combustion," presented at the 16th Annual ACERC Conference, Provo, Utah (March 14-15, 2002).

Lang, T., Hurt, R.H. "Char Combustion Reactivities for a Suite of Diverse Solid Fuels and Char-Forming Organic Model Compounds, " Proc. Comb. Institute, Vol 29 in press, 2003.

Hurt, R.H., Calo, J.M. "Semi-Global Intrinsic Kinetics for Char Combustion Modeling," *Combustion and Flame*, 125:1138-1149 (2001).

Lang, T., Hurt, R.H., Standard Combustion Reactivities of Chars from Diverse Solid Fuel Types, 2002 Australian Symposium on Combustion and Seventh Australian Flame Days, Adelaide, February 2002.

Zeng, D., M. Clark, and T. H. Fletcher, "High Pressure Coal Pyrolysis," poster presented at the 17th Annual ACERC Conference, Salt Lake City, Utah (February 20-21, 2003)

Several further papers are envisioned, but the team is still engaged in data gathering and analysis, and has not yet begun preparation of these further manuscripts.

Students Supported by Grant

Michael Clark, undergraduate research assistant at BYU

Andrew Lamb, undergraduate research assistant at Brown

Todd Lang, Ph.D. student at Brown

Diane Lopez, Ph.D. student at Brown

Dong Zeng, PhD student at Brigham Young University